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Henkel KGaADetergent powder with an ecologically-safe builder system, a special combination of surfactants and lipase

Abstract: Detergents containing finely-divided hydrated zeolite, alkali metal silicate, from 1 to 10% by weight of low-ethoxylated nonionic surfactants, from 1 to 10% by weight of higher-ethoxylated nonionic surfactants, and lipase, optionally anionic surfactants and peroxy bleaches as well as other additives and enzymes exhibit improved handling properties and improved retention of washing power.

Description

The invention relates to a detergent that contains zeolite and alkali metal silicate as builders, as well as surfactants, lipase and optionally a peroxy bleach.

Zeolites and in particular zeolite NaA are used as a phosphate substitute in detergents and cleaners, and mixtures of zeolite with alkali metal silicates and alkali metal carbonates as well as polymeric polycarboxylates are used to reduce the formation of scale. Complexing agents such as the salts of nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and the phosphoric acids are also used. Complexing agents, most of which are selective in action, have the task of eliminating heavy metal ions of which even trace amounts can have a seriously adverse effect on the washing process and in particular on bleaching action (Ullmann, 1987, Vol.8, pages 351-354). The phosphonates are known to counteract the precipitation of sparingly-soluble calcium salts and hence the scale formation and fabric-greying caused by the latter ("Einsatz von Phosphonaten in flüssigen Vollwachmitteln", [*use of phosphonates in heavy-duty liquid detergents*] M. Paladini, G. Schnorbus, Seifen-Öle-Fette-Wachse, vol. 115 (1989) pages 508-511). Also, the combined use of phosphonates and acrylic acid/maleic acid copolymers when compared with formulations containing only one of these two components results in a greater degree of fabric whiteness ("Einsatz von Phosphonaten in Haushaltswaschmitteln mit niedrigem Phosphorgehalt (1%)", [*use of*

phosphonates in domestic detergents with a low phosphorus content (1%)] M. Paladini, G. Schnorbus, *Seifen-Öle-Fette-Wachse*, vol. 114 (1988), pages 756-760.

European EP 0 291 869 describes phosphate-free builder combinations (builder systems) consisting of zeolite, aminoalkane polyphosphonate and/or polymeric polycarboxylates as well as 1-hydroxyethane-1,1-diphosphonate (HEDP), with certain weight ratios of the last-mentioned three components exhibiting a synergistic action in preventing the formation of scale on fibres.

Crystalline sheet sodium silicates have also been described as substitutes or partial substitutes for phosphates and zeolites. For example, European patent EP 164,514 discloses a phosphate-free builder combination that contains mainly crystalline sheet silicates of formula (I) $\text{Na}_2\text{MSi}_x\text{O}_{2x+1} \cdot y \text{H}_2\text{O}$, where M is sodium or hydrogen, x is a number between 1.9 and 4 and y is a number between 0 and 20 and preferred values of x are 2, 3 or 4. The sheet silicates can be used as water softeners either separately, or in detergent and cleaning compositions together with other builders such as phosphates, zeolite, other silicates, phosphonates and polycarboxylates.

For example, there are known from European patent applications EP 337,217 and EP 337,219 builder combinations for detergents that contain crystalline sheet silicates and optionally phosphates and polycarboxylates such as citrates, glyconates, NTA and/or iminodiacetates, but not zeolite. European patent application EP 405,122 describes a builder combination for fabric detergents, consisting of a mixture of zeolite and crystalline sodium sheet silicate in a ratio of from 4:1 to 1:4.

Enzymes are known as another component of detergents, for example enzymes such as lipase. For example European patent application EP 468,102 describes a detergent containing anionic (preferably ABS, ether sulphate, olefin sulphonate) and/or nonionic surfactants (preferably nonylphenyl, alkylpolyethoxylate) and lipase, preferably in an amount of from 10 to 100,000 LU/g, derived from *Pseudomonas plantarii*, as well as optionally builders.

European patent application EP 341,999 describes a surfactant composition containing anionic surfactants as well as nonionic surfactants selected from alkylene oxide adducts with fatty alcohols, fatty acids, fatty acid esters, fatty acid amides and fatty amines with at least 10 carbon atoms in the molecule, wherein the content of such nonionics, which contain a maximum of 5 alkoxyate groups per molecule, is at least 30%, and the total surfactant content is from 1 to 30% by weight, and lipase is present in an amount of from 0.005 to 100 LU/mg, calculated on the total surfactant composition.

German patent application DE 41 06 880 describes a detergent composition that contains a finely-divided hydrated zeolite, a solid alkali silicate as well as peroxy bleach, anionic, nonionic and zwitterionic surfactants, with the proviso that the detergent is free of water-soluble organic complexing agents of the substituted phosphonate class and is also free of polymeric carboxylates and alkali metal carboxylates. The nonionic surfactant is primarily a fatty alcohol with 5 ethylene oxide units.

Although the above-mentioned detergents with a builder system that is based on zeolite and Na silicate are particularly advantageous ecologically, they nonetheless require special production technologies in order to give them good handling properties, for example powder properties, without adversely affecting their performance properties at the same time. Particular difficulties are encountered when ethoxylated alcohols having a low degree of ethoxylation are used, because they can evaporate at the processing temperatures used because they have relatively low boiling points, with the result that the processability and performance of the detergent product may be impaired. A simple replacement of low-ethoxylated alcohols by higher-ethoxylated alcohols can in some cases cause a deterioration in washing performance.

The aim of the invention was to improve phosphate-free builder combinations for use in fabric detergent compositions with the objective of obtaining good detergent handling properties, in other words good powder properties, whilst retaining the detergent's performance properties. It has now been found surprisingly that these requirements are

satisfied by detergents that contain zeolite and Na silicate as builders, as well as a mixture of higher-ethoxylated and lower-ethoxylated surfactants together with lipase.

The invention relates to a detergent containing finely-divided hydrated zeolite, alkali metal silicate, nonionic surfactants and lipase, and optionally anionic surfactants and peroxy bleaches, as well as other additives, characterised in that it contains from 1 to 10% by weight of low-ethoxylated nonionic surfactants and from 1 to 10% by weight of higher-ethoxylated nonionic surfactants.

The finely-crystalline, synthetic, bound-water containing zeolite is preferably a detergent-grade, type A zeolite. Also useful are mixtures of zeolite NaA and NaX, the amount of zeolite NaX in these mixtures advantageously being less than 30%. Virtually no particles are larger than 30 μm and preferably at least 80% consists of particles that are smaller than 10 μm :

Useful zeolites have a mean particle size of less than 10 μm (measurement method: Fraunhofer diffraction; volume distribution mean value) and preferably between 1.5 and 4.5 μm , and more particularly between 2.0 and 4.0 μm . Their calcium-binding capacity, determined in the manner described in German patent application 24 12 837, is in the range from 100 to 200 mg CaO/g. The amount of finely-divided, in particular crystalline hydrated zeolite, contained in the composition is preferably from 30 to 65% by weight and in particular from 32 to 45% by weight, calculated on the water-free active material. The zeolite generally has a water content of from 17 to 25% by weight, preferably from 18 to 22 and in particular from 20 to 22% by weight.

The alkali metal silicates are added as solids and not as a solution. They can be amorphous or crystalline. Preferred alkali metal silicates are the sodium silicates, in particular amorphous sodium silicates, with a $\text{Na}_2\text{O} : \text{SiO}_2$ mole ratio of from 1:2 to 1:2.8. These amorphous alkali metal silicates are available in commerce for example under the name Portil® (Henkel).

As the crystalline silicates that can be used alone or in admixture with amorphous silicates, there are preferably used crystalline sheet silicates of formula (I) $\text{NaMSi}_x\text{O}_{2x+1} \cdot y \text{H}_2\text{O}$ wherein M is sodium, x is a number from 1.9 to 4, and y is a number from 0 to 20 and preferred values for x are 2, 3 or 4. Such crystalline sheet silicates are described for example in European patent application 164,514. Preferred crystalline sheet silicates of formula (I) are

those in which M is sodium and x is 2 or 3. Both β and δ -sodium disilicates $\text{Na}_2\text{Si}_2\text{O}_5 \cdot y \text{H}_2\text{O}$ in particular are preferred, with β -sodium disilicate being obtainable for example by the method described in international patent application WO 91/08171. The amount of alkali metal silicates contained in the compositions is preferably from 1 to 15% by weight and in particular from 2 to 8% by weight, calculated on the anhydrous active material. The weight ratio of zeolite to amorphous silicate, calculated on the anhydrous active materials, is preferably from 4 : 1 to 10 : 1. The crystalline sheet silicates are preferably used in amounts from 1 to 15% by weight and in particular from 2 to 7% by weight, the weight ratio of zeolite to crystalline sheet silicate, calculated on the anhydrous active material, being at least 5:1. In compositions that contain both amorphous as well as crystalline alkali metal silicates, the weight ratio of amorphous alkali metal silicate to crystalline alkali metal silicate is preferably from 1 : 2 to 2:1 and in particular from 1 : 1 to 2 : 1.

The detergent of the invention can contain up to 10% by weight and preferably from 1 to 5% by weight of sodium carbonate.

Polymeric carboxylates or polymeric carboxylic acids can also be present as builders. These polymeric carboxylates or carboxylic acids can be contained in the detergent of the invention in an amount of up to 2% by weight.

There can be used polymeric carboxylates or polymeric carboxylic acids having a relative molecular weight of at least 350 in the form of their water-soluble salts, particularly in the form of their sodium and/or potassium salts, such as polyacrylates, polyhydroxyacrylates, polymethacrylates, polymaleates and in particular copolymers of acrylic acid with maleic acid or maleic anhydride, preferably compounds with from 50 to 70% acrylic acid and from 50 to 100% maleic acid. The relative molecular mass of the homopolymers is generally in the range between 1000 and 100,000 and that of the copolymers is between 2000 and 200,000, preferably from 50,000 to 120,000, calculated on the free acid. An especially preferred acrylic acid-maleic acid copolymer has a relative molecular mass of from 50,000 to 100,000. Useful, but less preferred, compounds in this class are the copolymers of acrylic acid or methacrylic

acid with vinyl ethers, such as vinyl methyl ethers, vinyl esters, ethylene, propylene and styrene in which the amount of acid is at least 50% by weight.

Terpolymers can also be used as the polymeric carboxylates or carboxylic acids. These terpolymers contain, as monomers, two carboxylic acids and/or their salts and as the third monomer vinyl alcohol and/or a vinyl alcohol derivative or a carbohydrate. The first acid monomer or its salt is derived from a monoethylenically unsaturated C₃-C₈ carboxylic acid and preferably from a C₃-C₄ monocarboxylic acid, in particular from (meth)acrylic acid. The second acid monomer or its salt can be a derivative of a C₄-C₈ dicarboxylic acid, preferably a C₄-C₈ dicarboxylic acid, maleic acid being especially preferred. The third monomer unit is in this case formed by vinyl alcohol and/or preferably an esterified vinyl alcohol. Especially preferred vinyl alcohol derivatives are the esters of short-chain carboxylic acids, for example C₁-C₄ carboxylic acids, with vinyl alcohol. Preferred terpolymers contain from 60 to 95% by weight, in particular from 70 to 90% by weight of (meth)acrylic acid or (meth)acrylate, especially preferably acrylic acid or acrylate, and maleic acid or maleate, as well as from 5 to 40 % by weight, preferably from 10 to 30% by weight of vinyl alcohol and/or vinyl acetate. Particularly especially preferred are terpolymers in which the weight ratio of (meth)acrylic acid and (meth)acrylate to maleic acid or maleate is between 1:1 and 4:1, preferably between 2:1 and 3:1 and in particular between 2.1 (*sic*¹) and 2.5:1. These quantities and the weight ratios are calculated on the acids.

The second acid monomer or its salt can also be a derivative of an allylsulphonic acid substituted in the 2-position with an alkyl group, preferably a C₁-C₄ alkyl group, or an aromatic group preferably derived from benzene or benzene derivatives. Preferred terpolymers contain from 40 to 60% by weight, in particular from 45 to 55% by weight of (meth)acrylic acid or (meth)acrylate, more preferably acrylic acid or acrylate, from 10 to 30% by weight, preferably from 15 to 25% by weight of methallyl sulphonic acid or methallyl sulphonate and as the third monomer from 15 to 40% by weight, preferably from 20 to 40% by weight of a carbohydrate. The carbohydrate can be for example a mono, di, oligo or

¹ Presumably 2 : 1

polysaccharide, with mono, di or oligosaccharides being preferred, and sucrose being especially preferred. The third monomer is used to create predetermined breaking points in the polymer which make it degradable. The terpolymers used can be manufactured by any of the known conventional processes.

Preferably there are also used terpolymers which are neutralised either wholly or at least partially and in particular to the extent of more than 50%, calculated on the carboxyl groups present. Especially preferred is a completely neutralised terpolymer which thus consists of the salts of the monomeric acids, in particular the sodium or potassium salts of the monomeric acids, and vinyl alcohol or a carbohydrate. The terpolymers generally have a relative molecular weight of between 1000 and 200,000, preferably between 200 and 50,000 and in particular between 3000 and 10,000. They are generally used in the form of aqueous solutions, preferably in the form of 30-35 wt-% aqueous solutions. Especially preferred terpolymers are prepared by a method that is described in German patent applications P 42 21 381.9 and P 43 00 772.4.

The detergents of the invention can contain water-soluble complexing agents in the group of phosphonates. There are used the salts of polyphosphonic acids, such as the neutral sodium salts of for example 1-hydroxyethane-1,1-diphosphonate and diethylenetriamine pentamethylenephosphonate. The phosphonates can be used in amounts of up to 1.5% by weight, but preferably these additives are omitted, with the result that the detergents of the invention have a calculated phosphorus content of 0%.

As further components, the detergents and cleaners of the invention contain known compounds from the group of nonionic surfactants, and anionic and zwitterionic surfactants can also be present. The surfactants are contained in the detergents of the invention in a total amount of from 5 to 40% by weight, preferably from 5 to 30% by weight and in particular from 8 to 25% by weight.

As nonionic surfactants the detergent of the invention in particular contains low-ethoxylated and higher-ethoxylated nonionic surfactants. The nonionic surfactants can be present in an amount of from 2 to 25% by weight and preferably from 2 to 15% by weight.

The ethoxylated alcohols that are used as nonionic surfactants are derived from primary alcohols with preferably from 9 to 18 carbon atoms. The low-ethoxylated fatty alcohols contain on average from 1 to 6 moles and the higher-ethoxylated alcohols on average from 8 to 20 moles of ethylene oxide. The stated degrees of ethoxylation are statistical means which can be a whole or a fractional number for a given product. The alcohol can be linear or methyl-branched in the 2-position, or it can contain a mixture of linear and methyl-branched groups as is usual in oxo alcohol residues. However, there are especially preferred alcohol ethoxylates with linear residues derived from alcohols of native origin containing from 12 to 18 carbon atoms, for example from coconut, tallow or oleyl alcohol. The preferred lower-ethoxylated alcohols include for example fatty alcohols with from 12 to 18 carbon atoms and on average 3 to 5 EO units. Preferred higher-ethoxylated alcohols include for example fatty alcohols with from 16 to 18 carbon atoms with on average from 12 to 16 EO units, for example ethoxylated tallow alcohol. Preferred alcohol ethoxylates have a narrowed homologue distribution (= narrow range ethoxylates, NRE). The detergents of the invention contain from 1 to 10% by weight, preferably from 1 to 5% by weight of low-ethoxylated nonionic surfactants and from 1 to 10% by weight, and preferably from 1 to 5% by weight of higher ethoxylated nonionic surfactants. The lower-ethoxylated alcohols and the higher-ethoxylated alcohols are present in a weight ratio of from 10:1 to 1:10, preferably from 5:1 to 1:5 and especially preferably from 2:1 to 1:1.

Another class of nonionic surfactants that can be used in combination with the above-mentioned nonionic surfactants are alkoxyated fatty acid methyl esters for example as described in Japanese patent application JP 58/217598 or those obtained preferably by the method described in international patent application WO90/13533.

Also there can be used as further nonionic surfactants alkyl glycosides of general formula $RO(G)_x$ where R is a primary straight-chain or methyl-branched and in particular a 2-methyl branched aliphatic residue with from 8 to 22 and preferably from 12 to 18 C atoms, and G represents a glucose unit with from 5 to 6 C atoms, preferably glucose. The degree of oligomerisation x, which is indicative of the distribution of monoglycosides and oligoglycosides, can be any number between 1 and 10 and is preferably between 1.2 and 1.4. The alkyl glycosides can be used in an amount of from 0 to 5% by weight and in particular from 0.5 to 3% by weight in the detergent compositions of the invention.

As the anionic surfactants there can be used sulphates and optionally sulphonates, as well as soaps, preferably those derived from natural fatty acids or fatty acid mixtures. The anionic surfactants can be present in the compositions of the invention in a total amount of up to 15% by weight.

Useful surfactants of the sulphate class are the sulphuric acid monoesters of primary alcohols of natural or synthetic origin. As alk(en)yl sulphates there are preferred the sulphuric acid half esters of C_{12} - C_{18} fatty alcohols, for example coconut alcohol, tallow alcohol, lauryl, myristyl, cetyl and stearyl alcohol or C_{10} - C_{20} oxo alcohols, and secondary alcohols having this chain length. Also preferred are alk(en)yl sulphates of the aforesaid chain length containing a synthetic, petrochemically-derived straight-chain alkyl group, which have similar degradation properties to suitable compounds obtained from natural fat raw materials. For laundry purposes, C_{16} - C_{18} alk(en)yl sulphates are particularly preferred. It can be especially advantageous, particularly for machine detergents, to use C_{16} - C_{18} alk(en)yl sulphate in combination with lower-melting anionic surfactants and in particular with anionic surfactants that have a low Krafft point and exhibit little tendency to crystallise out at relatively low washing temperatures for example in the range from room temperature to 40 °C. In a preferred embodiment of the invention, the compositions contain mixtures of short-chain and long-chain fatty alkyl sulphates, preferably mixtures of C_{12} - C_{14} fatty alkyl sulphates or C_{12} - C_{16} fatty alkyl sulphates with C_{16} - C_{18} fatty alkyl sulphates. In a further preferred embodiment of the invention, there are used not only saturated alkyl sulphates, but also unsaturated alkenyl sulphates with an alkenyl chain length of preferably C_{16} - C_{22} . In this case,

mixtures of saturated, predominantly C₁₆ sulphated fatty alcohols and unsaturated, predominantly C₁₈ sulphated fatty alcohols are in particular preferred, especially those derived from solid or liquid fatty alcohol mixtures of the HD-Ozenol ® type (commercial product available from the Applicants). Weight ratios of alkyl sulphates to alkenyl sulphates of from 10:1 to 1:2 and in particular from about 5:1 to 1:1 are preferred. The compositions of the invention can contain up to 12% by weight of alk(en)yl sulphates and preferably they contain from 5 to 8% by weight.

The sulphuric acid monoesters of straight chain or branched C₇-C₂₁ alcohols ethoxylated with from 1 to 6 moles of ethylene oxide, such as 2-methyl-branched C₉-C₁₁ alcohols with on average 3.5 moles of ethylene oxide (EO) or C₁₂-C₁₈ fatty alcohols with 2-4 EO are also suitable. Because they are strongly sudsing materials, they are used only in relatively small amounts, for example from 1 to 5% by weight, in detergents.

If surfactants of the sulphonate class are used, then there can preferably be used C₉-C₁₃ alkylbenzene sulphonates, olefin sulphonates, that is to say mixtures of alkene and hydroxyalkane sulphonates and disulphonates, such as those obtained for example from C₁₂-C₁₈ mono-olefins with a terminal or internal double bond by sulphonation with gaseous sulphur trioxide followed by alkaline or acid hydrolysis of the sulphonation products. These surfactants can be used in the composition in amounts of up to 10% by weight, and preferably up to 5% by weight. However, sulphonate detergents can also be omitted without significantly impairing the washing performance.

Soaps can be used as further anionic surfactants, saturated fatty acid soaps such as the salts of lauric acid, myristic acid, palmitic acid and stearic acid, and soap mixtures derived from natural fatty acids for example coconut, palm kernel or tallow fatty acids being suitable. In particular there are preferred soap mixtures that consist of from 50 to 100% by weight of saturated C₁₂-C₁₈ fatty acid soaps and from 0 to 50% by weight of oleic acid soaps. Preferably the detergent compositions of the invention contain soaps in amounts of from 0.1 to 1.5% by weight.

The lipase contained in the detergent composition of the invention is an enzyme that is obtainable from microorganisms, in particular bacteria or fungi. Such enzymes are known for example from European Patent Applications EP 204,208, EP 214,761, EP 258,068, EP 407,225 and international application WO 87/859. Useful commercially-available lipases are for example Lipolase ® and Lipozym ®. Lipase is present in the compositions of the invention preferably in such quantities that the finished composition contains from 100 LU/g to 900 LU/g ("lipase-activity units" per gram, determined by the enzymatic hydrolysis of tributyrin at 30 °C and pH 7 by the method described in EP 258,068), more particularly from 150 LU/g to 800 LU/g and still more preferably from 200 LU/g to 450 LU/g.

The enzymes are used in the compositions of the invention in a form that is adsorbed on carriers, embedded in coatings, or as conventional granulates with inorganic and/or organic carriers, for example as described in German patent specification DE 16 17 232, German OLS Nos. DT 20 32 766 and DE 40 41 752, or European patent applications EP 168,526, EP 170,360, EP 270,608 or EP 304,331.

In addition to the lipase that is essential to the invention, the compositions of the invention can contain other enzymes, in particular those in the class of proteases, amylases, cellulases and their mixtures. Especially useful are enzyme materials that are derived from bacterial strains or from fungi, such as *Bacillus subtilis*, *Bacillus licheniformis*, and *Streptomyces griseus*. The enzymes can be adsorbed on carriers and/or embedded in coating substances to protect them from premature decomposition.

The enzymes can be contained separately in up to four separate particles, or they can be used in the form of multiple-enzyme granulates such as those for example described in international patent applications WO 90/09440 or WO 90/09428 and in the prior art cited in these documents.

The detergent compositions of the invention preferably contain peroxy bleaches and in particular peroxy bleaches combined with bleach activators. Among compounds that act as bleaches and deliver H₂O₂ in water, sodium perborate tetrahydrate and sodium perborate

monohydrate are of particular importance. Further useful bleaches are for example sodium percarbonate, peroxyphosphates, citrate perhydrates, as well as H_2O_2 -supplying peracid salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, and diperdodecanedioic acid. The detergent compositions preferably contain from 5 to 25% by weight and in particular from 10 to 20% by weight of bleaches, perborate monohydrate being especially preferred.

In order to obtain an improved bleaching action when washing at temperatures of 60 °C or below, bleach activators that form organic peracids with H_2O_2 can be incorporated in the preparations. Examples thereof are N- or O-acyl compounds, such as polyacylated alkylenediamines, in particular tetraacetylenediamine, acylated glycolurils in particular tetraacetylglycoluril, N-acylated hydantoins, hydrazides, triazoles, triazines, urazoles, diketopiperazines, sulphuryl amides and cyanurates, as well as carboxylic acid anhydrides, in particular phthalic anhydride, carboxylic acid esters, in particular sodium isononanoyl phenol sulphonate, and acylated sugar derivatives, in particular pentaacetyl glucose. The bleach activator can be coated in the known manner with coating materials or granulated optionally with the use of granulation aids, and it can if desired contain other additives, for example dyes. Preferably, a granulate of this kind contains more than 90% by weight, and in particular from 94% by weight to 99% by weight of bleach activator. Preferably there is used a bleach activator that forms peracetic acid under washing conditions.

Of these materials, tetraacetylenediamine (TAED) granulated with the assistance of carboxymethyl cellulose and having mean particle sizes of from 0.01 to 0.8 mm which can be obtained by the method described in European patent specification EP 037 026 and/or granulated 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT) which can be obtained by the method described in German patent specification DD 2 55 884, are especially preferred. The amount of bleach activators present in the bleach-containing detergent composition is in the usual range, preferably between 1 and 10% by weight and in particular between 3 and 8% by weight.

Other detergent components, which are present in an amount of from 0.1 to 5% by weight, depending on the composition of the detergent, include suds inhibitors, optical bleaches, fabric softeners, dyes and fragrances. Neutral salts in an amount of up to 20% by weight can also be present and their amount is preferably $\leq 0\%$ by weight.

The composition of the invention can also contain anti-redeposition agents in an amount of from 0.1 to 5% by weight. Anti-redeposition agents are used to keep the soiling that is removed from fibres suspended in the wash solution and so prevent its redeposition which causes fabrics to go grey. Useful for this purpose are water-soluble usually organic colloids, for example the water-soluble salts of polymeric carboxylic acids, size, gelatine, the salts of ether carboxylic acids or ether sulphonic acids, starch or cellulose, or salts of the acidic sulphuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also useful for this purpose. Soluble starch preparations and starch derivatives other than those mentioned above, for example degraded starch, aldehyde starches and the like, can also be used. Carboxymethylcellulose (Na salt), methyl cellulose, methylhydroxyethyl cellulose and their mixtures, as well as polyvinylpyrrolidone are preferred.

When they are used in machine washing processes it can be an advantage to add conventional suds inhibitors to the compositions. As suds inhibitors there are useful for example soaps of natural or synthetic origin with a high content of C_{18} - C_{24} fatty acids. Useful non-surfactant suds inhibitors are for example organopolysiloxanes and their mixtures with microfine, optionally silanised silicic acid, and paraffins, waxes, microcrystalline waxes and their mixtures with silanised silicic acid or bistearylethylenediamide. Mixtures of various suds suppressors are advantageous, for example mixtures of silicones and paraffins or waxes. Preferably, the suds inhibitors, in particular the silicone and/or paraffin-containing suds inhibitors, are bound to a granular water-soluble or water-dispersible carrier material. In particular, mixtures of paraffins and bistearylethylenediamides are preferred.

In a preferred embodiment, powder or granular detergents contain from 1 to 5% by weight of lower-ethoxylated nonionic surfactants, from 1 to 5% by weight of higher-ethoxylated nonionic surfactants, from 8 to 10% by weight of other surfactants, from 30 to 40% by weight

of a finely-divided hydrated zeolite with a mean particle size of from 2.0 to 3.8 μm , from 2 to 10% by weight of an amorphous sodium silicate with a $\text{Na}_2\text{O} : \text{SiO}_2$ molar ratio of from 2.0 to 2.8, or a mixture of the aforesaid amorphous sodium silicate with crystalline sheet silicate, preferably β -sodium disilicate or δ -sodium disilicate, from 18 to 30% by weight of peroxy bleach, preferably perborate, and from 1 to 3% by weight of a bleach activator, preferably TAED or DADHT, as well as from 100 to 900 LU/g of lipase.

The detergents of the invention can be prepared in the usual manner for example by mixing, granulating and/or spray-drying. The zeolite and alkali metal silicate builders can be incorporated separately into the compositions in the known manner and in any sequence.

Advantageously, the pourable powder or granular compositions consist of a dry, homogeneous mixture of at least two powder components, of which the first is a spray-dried granulate. It can be obtained by the conventional spray-drying of a slurry that contains at least the anionic surfactants and the zeolite in an aqueous suspension and optionally nonionic surfactants. Because of their heat sensitivity, bleaches such as perborate are not spray-dried together with the ingredients of the first powder component, but are mixed with the spray-dried product afterwards. Because zeolites and alkali metal silicates are known to be incompatible under spray-drying conditions, the alkali metal silicate powders are not spray-dried together with the zeolite-containing slurry. Equally, any sheet silicates that may be present are not spray-dried but admixed in granular form or adsorbed on a carrier that for example consists of sulphate and/or carbonate.

The compositions of the invention can be obtained most simply by mixing the enzyme particles in a conventional mixer, in particular a drum, roller, ribbon or tumbling mixer, and other optional powder components and if desired liquid or liquefied components which include in particular the nonionic surfactants as well as dyes and fragrances can be added by spraying them onto the aforementioned material. If in addition to the enzyme materials, the detergent composition of the invention is to contain other components, these components (provided they are heat-stable) are preferably converted in the known manner into a powder product by spray-drying an aqueous slurry, and mixed with the enzyme materials and

optionally other heat-sensitive components which in particular include the bleaches, for example alkali metal perborates or alkali metal percarbonate. It is also possible to incorporate the other components by admixing a granulate or extrudate containing them with the remaining components and this is preferred particularly when manufacturing detergents with a relatively high bulk density of preferably between 650 g/l and 900 g/l.

Examples

Granular detergents of the following composition were prepared and tested. The components listed in first to sixth place as well as zeolite NaA and sodium sulphate were mixed to make an aqueous spray slurry which was spray-dried in an experimental tower. The perborate, the bleach activator and the enzyme granulates were then mixed into the spray-dried product.

Exemplary formulations of the detergents used are set out in Table I in which Formulation A is a composition in accordance with DE 41 06 880, Formulation B is a comparative composition which corresponds neither to the prior art nor to the invention, and Formulations C and D are compositions in accordance with the invention.

Table 1
Examples of Formulations

Components, wt-%	A	B	C	D
Zeolite NaA (anhydrous active material) mean particle size 3.3 μm	38.0	38.0	38.0	38.0
Amorphous sodium silicate $\text{Na}_2\text{O} : \text{SiO}_2 = 1 : 2.0$	5.5	5.5	5.5	5.5
Soda	0	0	3	3
Na-polycarboxylate (Sokalan CP5 ®) ¹	0	0	0	2
Dehydol ® LST 80/20 ²	4.5	2.5	2.5	2.5
Dehydol ® TA 14 ³	0	2.0	2.0	2.0
Lipolase ® 30T ⁴	0	0	1.0	1.0
C ₁₂ alkylbenzenesulphonate (ABS)	7.5	7.5	0	0
C _{16/18} fatty alkyl sulphate (FAS)	0	0	7.5	7.5
Sodium perborate tetrahydrate	25.0	25.0	25.0	25.0
TAED	2.0	2.0	2.0	2.0
Balance (perfume, silicone oil, optical brighteners, sodium sulphate, water)				

- 1 Sokalan CP5 ® is an acrylic acid-maleic acid copolymer sodium salt, available commercially from BASF, Germany
- 2 Dehydol LST is a mixture of 80% of an ethoxylated C₁₂-C₁₈ fatty alcohol with on average 5 EO units and 20% of an ethoxylated C₁₂-C₁₄ fatty alcohol with on average 3 EO units.

3 Dehydol TA 14 is an ethoxylated C₁₆-C₁₈ fatty alcohol with on average 14 EO units

4 Lipolase 30T is a commercial product ex Novo, activity: 30,000 LU/g

The performance of the above formulations A, B, and D was tested. The test was conducted under practical conditions using domestic washing machines. The machines were filled with 3.5 kg of a normally-soiled domestic washload (bed linen, table linen, underwear) and 0.5 kg of test fabric. The test fabric comprised strips of standard cotton fabric (Krefeld Laundry Research Institute), grey cotton cloth, knitted fabric (cotton knit) and terry towelling. Washing conditions: tap water having a hardness of 23 °d (equivalent 230 mg CaO/l); main wash 8.0 g/l at 25 °C - 90 °C (heating time 60 mins, 15 mins at 90 °C); bath ratio (kg washload: litre wash solution in the main wash) 1 : 4; 5 rinses with tap water, spinning and drying.

The test fabrics were soiled with bleachable and enzyme-degradable soils. Using the detergent powder containing the builder combination of the invention gave comparable or better results for whiteness than the detergent powder that contained a standard builder combination (whiteness measured with a Zeiss reflectometer, 465 nm, brightener effect eliminated).

Soiling: grease/pigment soils.

Each test was repeated three times. The reflectance values set out below are the means of all the measurements. The residual grease content of the washed test fabric was determined. The values that were obtained are set out in the Table below. It is evident from this Table that the largest amount of grease was removed from the test fabric with the detergent of the invention.

Primary washing effect 40 °C	
Formulation	% reflectance makeup
A	68.6
B	64.7
D	68.5
± 2% R are significant	

Grease removal at 40 °C (meat dripping)	
Formulation	mg extracted residual grease
A	85.5
B	108.7
C	73.3

Claims

1. A detergent containing finely-divided hydrated zeolite, alkali metal silicate, nonionic surfactants and lipase, optionally anionic surfactants and peroxy bleaches as well as other additives, characterised in that it contains from 1 to 10% by weight of lower-ethoxylated nonionic surfactants and from 1 to 10% by weight of higher-ethoxylated nonionic surfactants.
2. A detergent according to Claim 1 characterised in that the lower-ethoxylated nonionic surfactants are derived from primary C₁₂- C₁₃ alcohols with an average of from 1 to 6 ethoxy units.
3. A detergent according to Claim 1 or 2 characterised in that the higher-ethoxylated nonionic surfactants are derived from primary C₁₆-C₁₈ alcohols with on average from 8 to 20 ethoxy units.

4. A detergent according to one of claims 1 to 3 characterised in that it contains from 1 to 5% by weight of lower-ethoxylated nonionic surfactants.
5. A detergent according to one of Claims 1 to 4 characterised in that it contains from 1 to 5% by weight higher-ethoxylated nonionic surfactant.
6. A detergent according to one of claims 1 to 5 characterised in that it contains from 100 to 900 LU/g and preferably from 150 to 800 LU/g.
7. A detergent according to one of Claims 1 to 6 characterised in that the lower-ethoxylated nonionic surfactants and the higher-ethoxylated nonionics are present in a weight ratio of from 5:1 to 1:5, and more particularly in a weight ratio from 2:1 to 1:1.
8. A detergent according to any one of claims 1 to 7 characterised in that it contains from 30 to 65% by weight of zeolite and from 1 to 15% by weight of alkali metal silicate, calculated on the anhydrous active material, the weight ratio of zeolite to alkali metal silicate, calculated on the anhydrous active material, being from 4 : 1 to 10 : 1.
9. A detergent according to any one of Claims 1 to 8 characterised in that it contains from 32 to 45% by weight of zeolite calculated on the anhydrous active material, from 2 to 8% by weight of alkali metal silicate, calculated on the anhydrous active material, and from 200 to 450 LU/g of lipase.
10. A detergent according to one of Claims 1 to 9 characterised in that it contains from 1 to 5% by weight of lower-ethoxylated nonionic surfactants, from 1 to 5% by weight of higher-ethoxylated nonionic surfactants, from 8 to 10% by weight of other surfactants, from 30 to 40% by weight of a finely-divided hydrated zeolite with a mean particle size of from 2.0 to 3.8 μm , from 2 to 10% by weight of amorphous sodium silicate with a $\text{Na}_2\text{O} : \text{SiO}_2$ mole ratio of from 2.0 to 2.8 or a mixture of amorphous sodium silicate with crystalline sheet silicate, preferably β -sodium disilicate or δ -sodium disilicate, from 18 to 30% by weight of peroxy bleaches,

preferably perborate, and from 1 to 3% by weight of a bleach activator, preferably TAED or DADHT, as well as from 100 to 900 LU/g of lipase.
